POTENTIAL OF OIL PALM LEAVES AS AN ADSORBENT FOR THE REMOVAL OF METHYLENE BLUE FROM AQUEOUS SOLUTION

SITI FATIN RAIHANAH BINTI MOHD SUHAIMI

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UNIVERSITI MALAYSIA PAHANG

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ABSTRACT

Coloring effluent from industrial activities may affect environmental and human health and with this concern, many methods have been studied to decolorize such effluent including physical, chemical and biological methods. Among the methods available, adsorption process is the most commonly used to remove dyes because of its low cost, simple design and easy to perform. Adsorption onto activated carbon has been used with great success. However, its high cost sometimes tends to limit its use. Therefore, many low-cost adsorbents have been developed for dye removal such as natural materials, industrial waste and agriculture waste. So, the aim of the present work was to investigate the feasibility of oil palm leaves (OPL), a solid waste, abundantly available in Malaysia, for the adsorption of methylene blue. Batch adsorption studies were conducted to evaluate the effects of adsorbent dosage (0.25-2.0 g/L), pH (2-8), initial concentration (50-400 mg/L), and temperature (30-70 ºC). The experimental data were analyzed by the Langmuir and Freundlich isotherms, and were found to follow the Langmuir isotherm model with coefficients of correlation $R^2 \geq 0.9512$ indicating that the ongoing process is chemical adsorption. Pseudo-first-order and pseudo-second-order kinetics models were tested with the experimental data, and pseudo-second-order kinetics was the best for the adsorption of MB by oil palm leaves with coefficients of correlation $R^2 \geq 0.998$ for all initial methylene blue concentrations studied. Thermodynamic parameters such as ΔH^o, ΔG^o and ΔS^o clearly indicated that the ongoing process is endothermic, spontaneous, and chemical in nature at 30-50^{o}C, while at 50-70^{o}C, the ongoing process is exothermic, spontaneous, and chemical in nature. The optimum conditions were achieved at 0.5 g/L of adsorbent dosage, pH 6, 400 mg/L initial dye concentration and 50 ^{o}C with maximum adsorption capacity of 694.6 mg/g. The adsorption of MB into the OPL was confirmed by SEM and FTIR for OPL before adsorption and after 50 min adsorption process. The results revealed that the (OPL) could be employed as a low-cost adsorbent for the removal of methylene blue from aqueous solution.

ABSTRAK

Sisa buangan berwarna dari aktiviti-aktiviti perindustrian boleh menjejaskan alam sekitar dan kesihatan manusia dan dengan kesedaran ini, banyak kaedah telah dikaji untuk menyahwarna sisa ini termasuklah kaedah fizikal, kimia dan biologi. Antara kaedah yang sedia ada, proses penjerapan adalah yang paling biasa digunakan untuk membuang pewarna kerana kosnya yang rendah, rekabentuk ringkas dan mudah untuk dilaksanakan. Penjerapan ke atas karbon teraktif telah digunakan dengan jayanya. Namun, kosnya yang tinggi kadang-kadang cenderung untuk menghadkan penggunaannya. Oleh itu, banyak penjerap kos rendah telah diperkenalkan untuk penyingkiran pewarna seperti bahan-bahan semulajadi, sisa perindustrian dan sisa pertanian. Jadi, kajian ini bertujuan untuk menyiasat kebolehan daun kelapa sawit (OPL), iaitu sisa pepejal, yang banyak didapati di Malaysia, untuk menyerap metilena biru. Kajian-kajian penjerapan kelompok telah dijalankan untuk menilai kesan dos bahan penjerap (0.25-2 g/L), pH awal (2-8) , kepekatan awal (50-400 ppm) dan suhu (30-70 ºC). Data kajian telah dianalisis oleh isoterma Langmuir dan Freundlich , dan didapati data mengikuti model isoterma Langmuir dengan pekali korelasi $R^2 \geq$ 0.9512 yang menunjukkan bahawa proses berterusan ialah penjerapan kimia. Model kinetik tertib-pseudo-pertama dan model kinetik tertib-pseudo-kedua telah diuji dengan data kajian, dan model kinetik pseudo kadar kedua adalah yang terbaik untuk penjerapan MB oleh daun kelapa sawit dengan pekali korelasi $R^2 \geq 0.998$ untuk semua kepekatan awal yang dikaji. Parameter termodinamik seperti ΔH^o, ΔG^o dan ΔS^o dengan jelas menunjukkan bahawa proses berterusan adalah endoterma, spontan, dan kimia dalam alam semula jadi pada suhu 30-50 ^oC, manakala pada suhu 50-70 ^oC, proses berterusan adalah eksoterma, spontan dan kimia dalam alam semula jadi. Keadaan optima telah dicapai pada 0.5 g/L dos bahan penjerap, pH 6, 400 mg/L kepekatan awal dan suhu 50 ^oC dengan kapasiti penjerapan maksimum 694.6 mg/g. Penjerapan MB ke dalam OPL telah disahkan oleh SEM dan FTIR bagi OPL sebelum dan selepas 50 min proses penjerapan. Hasil kajian menunjukkan bahawa OPL boleh digunakan sebagai bahan penjerap kos rendah untuk penyingkiran metilena biru dari larutan akueus.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF SYMBOLS

ºC	-	Degree Celcius
g	-	Gram
K	-	Kelvin
kJ	-	KiloJoule
L	-	Litre
mg	-	Milligram
mL	-	Millilitre
nm	-	Nano meter
%	-	Percent
W	-	Watt

LIST OF ABBREVIATIONS

MB	Methylene Blue
FTIR	Fourier-Transform Infrared Spectrometer
OPL	Oil Palm Leaves
SEM	Scanning Electron Microscopy

1 INTRODUCTION

1.1 Background

Dyes or coloring are organic compounds, which contain in their molecules color imparting chromophoric groups and acid or basic auxochromic groups responsible for dyeing ability due to the auxochromes, dye molecules can be permanently bonded with fibers or other materials. Chemical engineering aspects of dyes synthesis made essential part in development applied in chemical technology operation and constructions of specialist apparatuses. Besides their traditional use in textile, leather, paper, as well as the paint and varnish industries, dyes have become indispensable in other fields such as microelectronics, medical diagnostics and information recording techniques and they continue to be intensively developed (Hoffmann and Puszynski, 2009).

Dyes is the first contaminant to be recognized in water and has to be removed from wastewater before discharging it into water bodies. In the dyeing section of a textile industry, about 1000 L of water is used for every 1000 kg clothes processed. Discharged of such color effluents imparts color to the receiving water bodies such as rivers and lakes and will interfere with its intended beneficial use (Suraya, 2009). Thus, it is important to remove dyes from receiving water bodies.

Several methods have been used to remove the dye from wastewater such as reduction, precipitation, reverse osmosis dialysis exchange ions and the most popular is the adsorption. Adsorption process has the excellent efficiency in the removal of pollutants besides economical and simple in design, which make it applications, has expanded rapidly (Dabrowski, 2001). Usually, adsorption by activated carbon is widely used to removal dyes. This is because they have high capabilities for various kinds of dyestuffs but sometimes the uses of activated carbon is limited since they have a high costs (Bhatnagar and Jain, 2005).

Therefore, there is a need to find out much economical, effective, viable alternative adsorbent. As for that, natural materials, waste materials from industry or agricultural, and biosorbent can be obtained and employed as an inexpensive adsorbent. Oil palm leaves are usually being leftover or burned at the plantation area. In general, these materials have no economic value and in fact often create a serious problem of disposal. Thus utilizing oil palm leaves as an alternative and low-cost adsorbent would increase the economic value, help to reduce the cost of disposal and consequently can reduce the environmental pollution.

1.2 Motivation and Problem Statement

In the era of globalization, the request for dyes was increased since the industry of dyestuffs, textile, paper, leather, foodstuffs, cosmetics, rubber and plastics was growing rapidly. In our daily lives, dyes are also being used in anywhere like in food, clothing, wood, car, everyday equipments and others (Hoffmann and Puszynski, 2009). Most of the dyes and pigments are considered inert or non as toxic, although some are not totally innocuous. Interest in the environmental behavior of dyes is prompted primarily by concern over their possible toxicity and carcinogenicity, heightened by the fact that many dyes formerly were made of known carcinogens such as benzidine, which may be reformed as a result of metabolism. Methylene blue dyes have been shown to have high partition coefficients and solubility, suggesting significant potential for bioconcentration (Hunger, 2003).

Increasing the use of dyes in the industry indirectly cause environmental pollution, especially water. Textile and dyeing industry are among important sources for the continuous pollution of the aquatic environment. Because they produce approximately 5% of them end up in effluents. The textile and dyeing industries effluents are dumped in the sea, river or lake has bad impact on biological life various organisms in that area. Dyes are undesirable wastewaters because they contain high levels of chemicals, suspended solids, and toxic compounds. Colors that have reacted with metal ions can be highly dangerous toxic to aquatic aquatic flora and fauna and cause many water borne diseases (Vijayakumar *et al*., 2012).

Generally, dyes containing wastewaters can be treated in two ways, which are physical and chemical methods of dye removal (decoloration process) and by means of biodegradation. As for that, various chemical and physical methods have been proposed for the removal of dye from the effluent water. Those techniques are nanofiltration, electrokinetics coagulation, reduction, liquid-liquid extraction, ozonation, biological process and adsorption.

Among those, adsorption has been found to be the superior compared to the others techniques. It is due to its capability for efficiently adsorbing a broad range of adsorbates and its simplicity of design and economical, which make it applications, has expanded rapidly (Dabrowski, 2001). The adsorbents suitable for wastewater treatment plant are dead plant and animal matter called biomass; including charcoals, activated carbon, clays, soils, diatomaceous earth, activated sludge, compost, living plant communities, polymer synthesized from petrochemicals and inorganic salt coagulants.

Usually, adsorption by activated carbon is widely used to removal dyes. This is because they have high capabilities for various kinds of dyestuffs but sometimes the uses of activated carbon is limited since they have a high costs and difficult to regeneration (Bhatnagar and Jain, 2005). This has led many researchers to search for inexpensive and locally available adsorbents so that the process can become economically feasible.

Therefore, agricultural waste has been proposed as an adsorbent because it has the characteristics of ready availability, affordability, eco-friendliness and high uptake capacity for dyes. There are several agricultural waste which are used as adsorbent to removal dyes that have been studied and developed by researchers including palm ash (Abdulbari *et al*., 2006), oil palm empty fruit bunch (Manase, 2012), mangrove bark (Seey and Nordin, 2002), palm kernel coat (Oladoja and Akinlabi, 2009), Zea mays L (maize) husk (Jalil *et al*., 2012), coconut husk (Nazirah and Suhaili, 2011) and Acacia nilotica leaves (Prasad and Santhi, 2012).

Malaysia is one of the largest producers and exporters of palm oil in the world. With the increase in the production of palm oil, the amount of wastes generated including oil palm leaves is increasing enormously. One of the significant problems in the oil palm fruit processing is managing of the wastes generated during the processes (Husain, et al, 2003). It has been reported that, in January 2006 itself, the total wastes that include oil palm leaves, oil palm fronds, empty fruit bunch and oil palm shell from the oil palm industries are 3.96 million tons (Suraya, 2009). In addition, oil palm leaves have no economic value and in fact often create a serious problem of disposal. Thus utilizing oil palm leaves as an alternative and low-cost adsorbent would increase the economic value, help to reduce the cost of disposal and consequently can reduce the environmental pollution.

The basic components that included in the oil palm leaves are lignin, cellulose and hemicelluloses with polyphenolic groups (Grassi *et al*., 2012). These materials are most excellently to removal dyes from the wastewater through sorption mechanisms. Cellulose for example show a potential sorption capacity for various pollutants. Thus, it is expected that the cellulose components in the oil palm leaves will become an active sites for the adsorption of methylene blue from aqueous solution.

1.3 Objective of the study

The research was conducted to investigate the potential of oil palm leaves as an adsorbent for the removal of methylene blue from aqueous solution.

1.4 Scopes of the study

The scopes of this study were focusing on the:

i. Effect of adsorbent dosage (0.25-2 g/L).
ii. Effect of initial concentration (50-400 ppm).
iii. Effect of initial pH (2-8).
iv. Effect of initial temperature (30-70 ºC).
v. Kinetic, isotherm and thermodynamic of adsorption.

2 LITERATURE REVIEW

2.1 Dyes

Dyes can be described as colored, ionizing and aromatic organic compounds. Generally, they can be described as a coloured substance that has an affinity to the substrate to which it is being applied. Dyes show the characteristics of intense color, solubility and fastness since they are complex unsaturated aromatic compounds. The dye is generally applied in an aqueous solution, and may require a mordant to improve the fastness of the dye on the fiber.

The developments of industrial methods of manufacturing fabrics brought about a rapid increase in demand for coloring substances. Besides that, dyes are used everywhere in our daily life like in food, fabrics, car, wood, newspaper, books, plastic products, decorative materials, films, everyday equipment and other. Their importance has grown in almost every area of an economic activity (Hoffmann and Puszynski, 2009).

2.1.1 Classification of Dyes

Dyes are classified based on the fiber to which they may be used and the chemical properties of each coloring. Before dyes are categorized, it must be noticed that each class has a particular dye chemistry, structure and how the particular bond. Dyes can react chemically or physically with the substrates that make up firm bonds in the process. Dyes are divided into nine types, namely dyes azoic dyes, acid dyes, basic dyes, direct dyes, reactive dyes, mordant dyes, solvents dyes, sulfur dyes and vat dyes (Christie, 2007).

Azoic dyes are dispersed in water and are used for most synthetic fibers. Since most of the other classes of dye quickly deficiency in red dye, these coloring is used mainly for the bright red colors in dyeing and printing. They are used to rarely on nylon, cellulose, cellulose acetate, and acrylic fibers but used to mostly on polyester. Azoic dyes, with fixation rates of 80 to 90 percent requiring an additional factor likes carriers of coloring, pressure, and heat to penetrate the synthetic fibers (Snowden, 1995).

Acid dyes are a very bigger and substantial group of dyestuff. These type was covered in brief by (Hendrickx and Boardman, 1995) which are the acid dyes containing sulfonic groups. They attach to organic fibers under acidic condition. Usually, these colorings are used in dyeing nylon, silk and wool but it rarely used for dyeing cotton besides paper, leather, ink-jet printing, food, and cosmetics.

Basic dyes are water-soluble and resulting colored cations in solution. For this reason, they are often referred to as the cationic dye (Hunger, 2003). Dyes are coloring derived from the first synthetic coal-tar derivatives. Without the help from mordant and agent, basic dyes originally used to color the wool, silk, linen, hemp and others. But, by using mordant like tannis acid, basic dyes have been used on cotton and rayon. These dyes give attractive colors with exceptional fastness to acrylic fibers. Today, the basic colouring no longer be used for any level of cotton or linen and seldom on wool but by the reasons of they are cheap, they are used for hemp, jute and similar fibers. Now, basic dyes used are focused on acrylics (Hoffmann and Puszynski, 2009).

Direct dyes are water-soluble anionic dyes because it consist sulfonic acid group that has a high linking for cellulosic fibers. These dyes have been used from a neutral or slightly alkaline, which consists of additional electrolyte. By looking the aspect of easiest to use and the low-priced in their beginning and operation charge, direct dyes are most suitable coloring even there are tradeoffs in the dyes' shade range and wet fastness (Corbman, 1975). Direct dyes generally were applied on cotton, linen, rayon, wool, silk and nylon.

Reactive dyes are successfully used on coloring cotton, wool, silk, and nylon. Reactive dyes form a covalent bond with the fiber under influence of heat and pH (alkaline). Reactive dyes have more advantages than direct dyes since their chemical structures are much clear, their absorption spectra show thinner absorption bands and the dyeing are much brighter. These dyes are made from azo, triphendioxazine, phthalocyanine, formazan, and anthraquinone (Christie, 2007).

Mordant are known as metal salt. Although other metallic salt mordants available, alum still used for ancient dyes. Mordant dyes are applied in conjunction with chromium salts like sodium or potassium. Some acid dyes that have the capability to form complexes with metal ions needed mordant as fixing agents to upgrade the color fastness. Dyeing consists in prep adding of the substrate with metal salts and then applying dyes forming insoluble complexes with the metals, which are anthraquinone, nitroso, xanthene, oxazine, triphenylmethane and azo dyes (Hoffmann and Puszynski, 2009). Commonly, these dyes are used for wool, leather, and anodized aluminium.

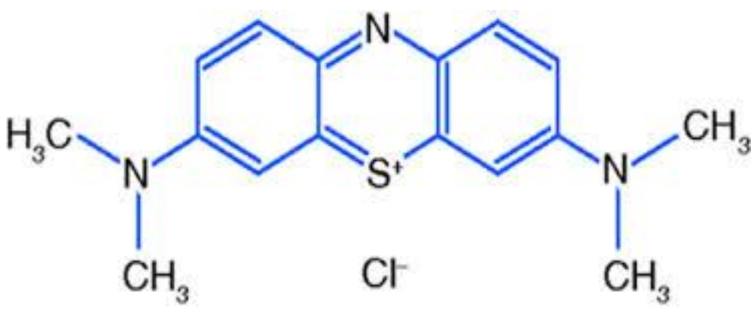
Solvent dyes are good used for dyeing plastics, gasoline, varnishes, lacquers, stains, inks, fats, oils, and waxes. Method applications for solvent dyes are dissolution in the substrate. The principal chemical classed are azo, triphenylmethane, anthraquinone, and phthalocyanine (Hunger, 2003).

Sulfur dyes are used for cotton, linen, and rayon but these dyes have given not brightly colored on the materials. These dyes act as reducing agent when dyes are applied for cotton from an alkaline reducing bath with sodium sulfide. Solvent dyes are very small group of dyes compared with the other types of dyes. These dyes are excellent wash fastness properties and the low cost making this class important dyeing in term of the economy although they are a small group of dyes. Nevertheless, they are not very suitable in term of environmental condition (Hunger, 2003). These dyes followed the method application of aromatic substrate vatted with sodium sulfide and deoxidized to insoluble sulfur-containing products on fiber.

The term vat comes from the old indigo method dyeing in a vat: indigo had to be reduced to light form (Michael, 1990). Vat dyes are water insoluble. Usually these dyes are treated with alkaline reducing agents, commonly with sodium hydrogensulfite before they are applied to cellulosic fibers as leuco salts. Anthraquinone (including polycyclic quinones) and indigoids are the principle chemical in making of vat dyes. Generally, these dyes are applied on cotton, linen, rayon, wool, silk, but they are rarely used on nylon.

2.1.2 Methylene Blue dye (MB)

Table 2.1: Properties of Methylene Blue (MB) (PubChem website)

Methylene Blue (MB)


Chemical formula	$C_{16}H_{18}ClN_3S$
IUPAC name	(7-dimethylaminophenothiazin-3- ylidene)- dimethyl- azanium chloride, Methylthioninium chloride
Other names	Methylthioninium chloride, Basic blue 9, Chromosmon, Swiss Blue, Methylene Blue N, 61-73-4
Molecular Mass	319.85 g/mole
Melting Point	100-110 ^oC
Vapor Pressure	1.30×10^{-7} mmgH
Solubility in Water	43 600 mg/L
Soluble in Organic	Soluble in glacial acetic acid and glycerol, insoluble in xylene and oleic acid, in ethanol 2%, and in acetone 0.5%.
Nature	Powder form
CAS No.	61-73-4

Among the various classes of dyes, basic dyes are the brightest class of soluble dyes used by the textile industry, as their tinctorial value is very high. Methylene blue is a basic dye by nature. MB is a basic dye which is widely used in textile, trace, biological laboratory purpose. MB is a blue dye used to dye wool, silk and tannin mordant cotton (Christie, 2007).

A MB can cause eye bum, and if swallowed, its causes irritation to the gastrointestinal tract with symptoms of nausea, vomiting and diarrhea. It may also cause methemoglobinemia, cyanosis, convulsions and dyspnea if inhaled (Senthilkumaar *et al.*, 2005). It is also can cause formation of toxic carcinogenic breakdown products.

2.2 Adsorption

Adsorption is the process that substances accumulates at the interface of two phase like gas-liquid, gas-solid, liquid-liquid or liquid-solid interface (Grassi *et al.*, 2012). Adsorbent and adsordate are the mainly component that include in adsorption process.

Adsorbate is the substance being adsorbed on the surface of adsorbent whereas adsorbent is adsorbing materials or the substance that accumulates on the surface of a solid or a liquid. The constituents of adsorbates and adsorbents will specify their properties.

Attraction force between adsorbate and adsorbent occur when the force attractions Van der Waal are weak or chemical bonds have strong attraction force. Adsorption can be divided into two types according to the attraction force between two components, adsorbate and adsorbent. The types of adsorption are physisorption and chemisorptions. Table 2.2 below show the differences between physisorption and chemisorptions.

Table 2.2 : Differences between physisorption and chemisorptions (Butt *et al.*, 2003 and Myers, 1999)

Physisorption	Chemisorption
• Involves van der Waals force between adsorbate and adsorbent.	• Involves formation of chemical bonds between adsorbate and adsorbent
• Low enthalpy of adsorption	• High enthapy of adsorption
• May formed multi-molecular layer	• Monolayer is formed
• Reversible process	• Irreversible process
• A general phenomenon, occurs in any solid/fluid or solid/gas system.	• A highly specific process
• Perturbation of the electronic states of adsorbent and adsorbate is minimal	• Changes in the electronic states may be detectable by suitable physical means.
• Typical binding energy is about • 10–100 meV.	• Typical forms bonding with • energy of 1–10 eV
• No activation energy is invovled	• Often involves activation energy
• Equilibrium can be achieved • quickly	• May take a longer time to • achieve equilibrium

Generally, the process that involve in adsorption is energy release. In nature, the most adsorption process is exothermic. Since adsorption process are spontaneous, so its free energy change and entropy change is negative value because during the adsorbate get linked to the surface of the adsorbent, the adsorbate molecules lose their translation freedom (Butt *et al.*, 2003).

Adsorption is widely used in industrial applications and useful most natural physical, biology and chemical systems. Lately, applications for adsorption have expanded rapidly especially for wastewater treatment besides for activated charcoal and synthetic resins. Their efficiency in the removal of pollutants, economical and simple in design makes the adsorption process become famous.

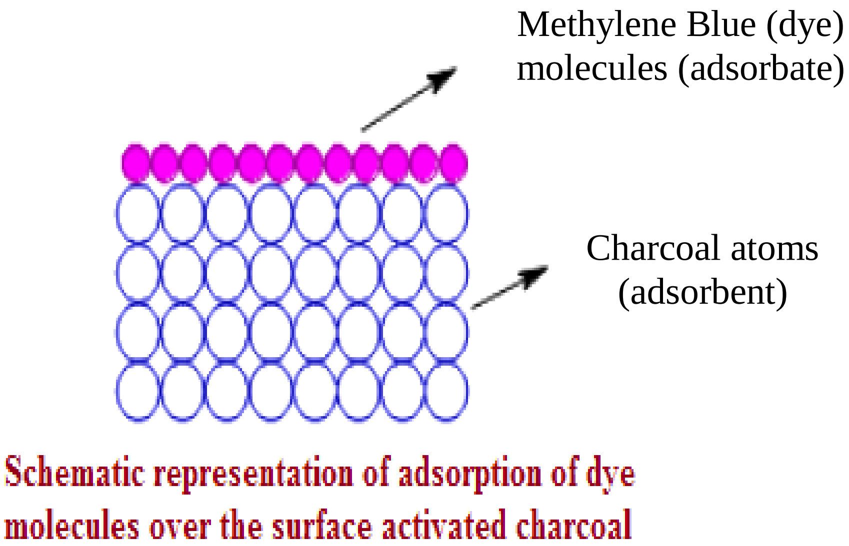


Figure 2.1 : Schematic representation of adsorption mechanism (Kumar, 2012)

2.2.1 Adsorption Kinetics

Several kinetic models have been proposed in order to examine the controlling mechanism of adsorbate adsorbed by adsorbents. Usually, the controlling mechanisms that have been examined are mass transfer, diffusion control and chemical reaction. In practical operation, analysis of adsorption rates is very essential especially in terms of system design (Wu, 2002). The simple kinetic analyses of adsorption are the pseudo-first-order model and the pseudo-second-order model.

2.2.1.1 Pseudo-First-Order Model

Lagergren's first order rate equation or also known as pseudo-first-order model is the earliest known predict dye adsorption kinetics. According to (Lagergren, 1898), the pseudo first order equation is expressed by the following equation:

$$\frac{dq}{dt} = k_1^{'}(q_e - q_t) \qquad (1)$$

Where q_e is the amount of solute adsorbed at equilibrium per unit weight of adsorbent (mg/g), q_t the amount of solute adsorbed at any time (mg/g) and k_1 is the adsorption constant (min^{-1}).

Integrating equation above for the boundary conditions t = 10 to $t = t$ and $q_t = q_t$ gives:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \qquad (2)$$

In order to obtain the rate constants k_1, the slope of the linear plots of log ($q_e - q_t$) against t be calculated.

2.2.1.2 Pseudo-Second-Order Model

Ho and Mckay (Ho and Mckay, 1998) proposed a second order model for the sorption of divalent metal ions onto peat particles based on the adsorption capacity of the adsorbents. These models were proposed with the goal of differentiating the kinetics of a second-order rate expression based on the adsorbent concentration. The models that are based on the solute concentration and represent a pseudo-second-order rate expression.

The pseudo-second-order kinetic equation is described as:

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \qquad (3)$$

Where k_2 is the rate constant of pseudo-second-order adsorption (g/mg min). Integrating equation above for the boundary conditions t = 0 to $t = t$ and $q_t = q_t$ gives:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \qquad (4)$$

or equivalently

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \qquad (5)$$

Where k_2 and q_e can be obtained from the intercept and slope of the plot of t/q_t verses t (Wu, 2001).

2.2.2 Isotherm Equation

Adsorption isotherms or also known as equilibrium data explain how adsorption occurs between adsorbate and adsorbents and also give some essential information to develop the equation. This equation can be used for a certain purpose.

There are several equilibrium isotherms with different models were proposed in other to describe the adsorption process. Langmuir and Freundlich are suitable isotherm models in order to investigate the adsorption behaviour. The Langmuir isotherm is restricted for monolayer adsorption only whereas the Freundlich isotherm is based on empirical equation.

2.2.2.1 Langmuir Isotherm Equation

The Langmuir adsorption isotherm is familiar and mainly used in process of adsorption. However, the Langmuir adsorption isotherm is suitable for single-layer adsorption only (Grassi *et al.*, 2012). The theoretical Langmuir isotherm (Langmuir, 1918) takes the following simplified form:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{6}$$

Equation 6 can be rearranged to a linear form:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}} \tag{7}$$

Where q_e is the equilibrium adsorption capacity (mg/g), C_e is the equilibrium liquid phase concentration (mg/L), q_m is the maximum adsorption capacity, (mg/g), K_L is Langmuir equilibrium constant, (L/mg). These constants can be evaluated from the intercept and the slope of the linear plot of experimental data of C_e/q_e versus C_e, respectively.

The variation of the surface and porosity of the adsorbent can give influence to the adsorption capacity. A higher adsorption capacity is due by increasing surface area and pore volume. A dimensionless constant separation factor or called as the equilibrium parameter can showed the essential characteristics of the Langmuir isotherm (Langmuir, 1918). The equilibrium parameter, R_L can be developed as follow :

$$R_L = \frac{1}{1 + K_L C_o} \tag{8}$$

Where K_L is Langmuir equilibrium constant, (L/mg), C_o is initial concentration (mg/L) and R_L values indicating the type of isotherm. The R_L value indicates the adsorption to be unfavourable (R_L > 1), linear (R_L = 1), favourable (0> R_L > 1) or irreversible (R_L = 1).

2.2.2.2 Freundlich Isotherm Equation

The Freundlich isotherm equation is an empirical relationship to explain about the adsorbate adsorb to the adsorbent surface. In addition, this equation also used to describe the heterogeneous systems, reversible adsorption and characterized by heterogeneity factor, 1/n. Contrary to the Langmuir isotherm equation, the Freundlich isotherm equation not restricted to the formation of the monolayer only because this isotherm is suitable for a highly heterogeneous surface (Grassi *et al*., 2012).

The ordinary adsorption isotherm is expressed by the following equation:

$$q_e = K_F C_e^{\frac{1}{n}} \qquad (9)$$

The Freundlich equation also can be written in the following linear form:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \qquad (10)$$

C_e is the equilibrium liquid phase concentration (mg/L), q_e is the equilibrium adsorption capacity (mg/g), K_F is Freundlich equilibrium constant (L/mg) and n is the constant for intensity whereby values n > 1 represent favourable adsorption condition. The intercept value of K_F and the slope of 1/n can be obtained by plotting a linear graph of log q_e versus log C_e.

2.2.3 Thermodynamic Parameters

Spontaneity of a process can be determined by thermodynamic parameters. Thermodynamic parameters such as enthalpy change (ΔH^o), free energy change (ΔG^o), and entropy change (ΔS^o) can be estimated using equilibrium constants changing with temperature. During spontaneous process, increasing temperature will decrease the values of (ΔH^o) and (ΔG^o). The relationship between the thermodynamic equilibrium constant and the Gibbs free energy is given by the Van't Hoff equation below (Al-Omari, 2007):

$$\Delta G^o = -RT\ \mathrm{In}K_a \qquad (11)$$

and

$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad (12)$$

Combination of both equations and taking the natural logarithms of both sides give:

$$\text{In } K_a = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \qquad (13)$$

Where ΔG^o is the free energy change (kJ/mol), ΔH^o the change in enthalpy (kJ/mol), ΔS^o is the entropy change (kJ/mol K), T is the absolute temperature (K) and R is the universal gas constant (0.8314 x 10^{-3} kJ/mol K). $K_a = (q_e / C_e)$ is a single point or linear sorption distribution coefficient.

2.3 Adsorbent Material

2.3.1 Introduction of Adsorbent

Many types of adsorbent are used to remove dyes from wastewater and the most popular adsorbent is the activated carbon. Activated carbon has a capability to adsorb many types of dyes with a high adsorption capacity but it is expensive to be used in developing countries.

Consequently, many low-cost adsorbents that have been made or developed must have the characteristic either basis of their availability or depending on their nature (Grassi *et al*., 2012). Oil palm leaves is the right choice to used as adsorbent because it readily available resources and cheap besides have excellent adsorption abilities for organic pollutants.

2.3.2 Oil Palm Leaves as Alternative Adsorbent

Malaysia is one of the largest producers and exporters of palm oil in the world. With the increase in the production of palm oil, the amount of wastes generated including oil palm leaves is increasing enormously. Oil palm leaves have no economic value and in fact often create a serious problem of disposal. Thus utilizing oil palm leaves as an alternative and low-cost adsorbent would increase the economic value, help to reduce the cost of disposal and consequently can reduce the environmental pollution (Grassi *et al*., 2012).

The basic components that included in the oil palm leaves are lignin, cellulose and hemicelluloses with polyphenolic groups (Grassi *et al*., 2012). These materials are most excellently to removal dyes from the wastewater through sorption mechanisms. Cellulose for example show a potential sorption capacity for various pollutants. This was observed by the absorption of methylene blue onto Sumac Leaves (Dülger *et al*., 2013). Before methylene blue adsorption, the surface of Sumac Leaves is smooth and porous whereas after methylene blue adsorption, the surface has become rough and corroded. It is evident that cellulose has a potential sorption capacity for various pollutants. Thus, it is expected that the cellulose components in the oil palm leaves will become an active sites for the adsorption of dyes from aqueous solution.

2.4 Previous Study

2.4.1 Previous study using oil palm as adsorbent

Fairus *et al.,* (2007) studied the application of palm oil fibre in removing methylene blue from aqueous solution. Color was effectively been removed at all selected pH, and the increase in activated carbon dose showed an increase in the removal's percentage. The adsorption capacity was rising with increasing of initial dye concentration. The adsorption equilibrium for colour was reached after 90 minutes of contact time. The adsorption followed both Langmuir and Freundlich isotherms.

In addition, Sidik *et al*., (2012) investigated the potential of lauric acid (LA) modified oil palm leaves (OPLsLA) for the removal of crude oil from the aqueous solution. They reported that equilibrium was achieved at about 60 minutes of contact time and the optimum pH for adsorption was around pH 4-5. The best dosage for adsorption was 1 to 2 g/L. The result maximum adsorption capacity of 1176.93 mg/g at 303K. The adsorption process was followed the pseudo second-order kinetic model and Langmuir isotherm. Results obtained indicate that palm oil fibre could be employed as a low cost alternative to commercial activated carbon in wastewater treatment for dye removal.

The comparison of adsorption capacities of oil palm leaves and corn husk for adsorption of Methylene Blue dye was studied by Suraya (2009). She reported that the best adsorption for both leaves was obtained at pH 6. The amount of dye adsorbed decreased with rising temperature from 310 K to 360 K, indicating the exothermic nature of the process.The adsorption kinetic and equilibrium fitted the pseudo second-order and Langmuir isotherm models respectively. The maximum capacity obtained was 315.6 mg/g for oil palm leaves and 304.6 mg/g for corn husk. Results obtained indicate that oil palm leaves could be employed as a low cost alternative to commercial activated carbon in wastewater treatment for dye removal.